



Recovery of Ni, Co and rare earths from spent Ni–metal hydride batteries and preparation of spherical Ni(OH)₂

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ABSTRACT

A hydrometallurgical procedure has been developed for the separation and recovery of nickel, cobalt and rare earths (RE) from spent Ni–MH batteries. In the process of separation and recovery, the positive and negative electrode materials were merged and leached with 3 M H₂SO₄ at 95 °C. In this stage, about 94.8% of rare earths were separated from other metals due to the low solubility of RE₂SO₄ at relatively high temperature. Then iron, zinc and manganese (together with the remaining 5.2% rare earths) were almost completely separated from nickel and cobalt by solvent extraction with 20% P204. Rare earths in the organic phase were recovered by stripping with 2 M HCl after scrubbing Zn and Mn. Most rare earth sulphates remaining in the leach residue were transformed to RE(OH)₃ by treatment with NaOH and then redissolved from the filter cake as RECl₃ by using the rare earth strip liquor and additional HCl. Cobalt was easily separated from nickel by solvent extraction with 20% Cyanex 272 and pure cobalt and nickel sulphates were recovered from evaporation of the strip liquor and raffinate respectively. Finally, spherical nickel hydroxide powder was synthesized from the pure nickel sulphate, which is an important starting material for Ni–MH batteries. The overall recovery efficiency for rare earths, cobalt and nickel exceeded 98%.

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1. Introduction

Ni–MH batteries have been applied widely in many fields since they were commercialized in 1990. Their electrodes consist of foamed-nickel or copper plating strip as substrate and nickel hydroxide and AB₅-type hydrogen-storage alloy as active electrode material. Therefore Ni–MH batteries contain valuable metals in which the average content of Ni, Co and light rare earths is about 30% 4% and 10% respectively (Zhang et al., 1999). The output of Ni–MH batteries is steadily rising due to their low cost, high electrochemical capacity, quick charging capability, long cycle life, good security, good environmental compatibility, wide range of usable temperature, etc. It is estimated that the Ni–MH batteries will occupy ~30% of the international battery market in 2010 (Tzanetakis and Scott, 2004a,b) and have an average service life of about two years. In 2005, it was determined that the total number of spent Ni–MH batteries reached one billion, in which there exists about 7500 ton Ni, 1000 ton Co and 2500 ton light RE. Because the arbitrary dumping of spent Ni–MH batteries could lead to serious heavy metal pollution, the recovery of valuable metals from spent Ni–MH batteries has received much attention (Espinosa et al., 2004; Bertuol et al., 2006; Muller and Friedrich, 2006; Rabah et al., 2008).

Many hydrometallurgical processes have been developed to recover metals from spent Ni–MH batteries in recent years. Tenorio and Espinosa (2002) used ore-dressing methods to recover the nickel-based alloy from Ni–MH batteries whilst Wang et al. (2002) regenerated the hydrogen-storage alloy from Ni–MH batteries, whose structure and electrochemical properties could be restored. Zhang et al. (1998, 1999) reported a hydrometallurgical process for the separation and recovery of metal values such as nickel, cobalt and rare earths from spent Ni–MH batteries. In their research work, the electrode materials were dissolved in 2 M H₂SO₄ at 95 °C with a leach efficiency of 97% Ni, 100% Co and 96% RE. The rare earth values were recovered from the leach liquor by solvent extraction with 25% D2EHPA, followed by precipitation with oxalic acid and calcination. The cobalt and nickel in the raffinate were then separated by 20% Cyanex 272 and recovered as oxalates by the addition of oxalic acid. More recently, Tzanetakis and Scott (2004a,b) also used D2EHPA to extract rare earths from the leach solution, then nickel and cobalt powders were separated and recovered through electrochemical deposition.

Because the solubilities of rare earth sulphates are low, especially at higher temperature, a large ratio of liquid to solid must be used to ensure a high leach recovery of rare earths, which makes the final nickel concentration low. This leads to large amounts of wastewater and high energy consumption.

This work develops a facile and low-cost flowsheet to recover and separate rare earth, nickel and cobalt from the electrode materials of spent Ni–MH batteries. Higher concentrations of H₂SO₄ and lower ratios of liquid to solid were adopted in the leaching step, which

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precipitated most of the rare earths as sulphates in the leach residues. Consequently, the leach liquor contained relatively low concentrations of rare earths and high concentrations of nickel, which decreased the consumption of extractant and the emission of wastewater. Subsequently, a high-density spherical $\text{Ni}(\text{OH})_2$ with wide size distribution was prepared from the concentrated nickel solution by the “controlled crystallization method”. This material can be used to produce the positive active material of Ni–MH batteries and thereby realize the recycling of nickel from Ni–MH batteries.

2. Experimental

2.1. Materials

Cylinder shaped Ni–MH batteries, used in this work, were provided by a battery plant. The commercial extractants employed, bis-(2-ethylhexyl) phosphoric acid (P204) and bis-(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) were purchased from Luoyang Zhongda Chemical Co. Ltd and Cytec Industries, respectively. These extractants were utilized without any further purification with kerosene diluents. All other reagents were of analytical reagent grade.

The spent Ni–MH batteries were cut to remove the shells. Positive materials, negative alloy powders and foamed-nickel matrixes were taken out. Then, the mixed electrode materials were washed by water to remove alkali electrolytes. The cells weighed an average of 28.9 g, each containing 19.5 g mixed electrode materials assaying about 61.2% Ni, 5.1% Co, 1.7% Mn, 2.2% Zn, 15.4% RE, 0.35% Fe.

2.2. Leaching

100 g mixed powders of electrode materials were leached in 750 mL of 3 M H_2SO_4 with stirring for 4 h at different temperatures (30 °C–95 °C). After leaching, the insoluble residue was filtered hot and washed with ~250 mL hot water, giving 1 L of leach solution.

2.3. Solvent extraction

Extraction and stripping tests were carried out in a micro mixer-settler whose effective capacity of mixing chamber and clarifying chamber were 0.64 L and 1.92 L respectively. All experiments were performed at room temperature with the mixing speed set at 80 rpm. Concentrated NaOH was used for the saponification of the extractants (to an extent of 65%) and adjustment of pH values. The concentrations of P204 and Cyanex 272 in kerosene were both 20% by volume.

2.4. Crystallization of rare earth, nickel and cobalt product

Most of rare earths existed as sulphates in the leach residue and were thoroughly precipitated as $\text{RE}(\text{OH})_3$ after treatment with alkali. The precipitates were redissolved by the HCl strip liquor of rare earths and additional HCl. Rare earth chlorides were crystallized from the filtrate through evaporation.

After rare earth and impurity removal and solvent extraction separation of Co and Ni, pure CoSO_4 and NiSO_4 solutions were obtained, allowing CoSO_4 and NiSO_4 hydrates to be crystallized from the mother liquid through evaporation.

2.5. Preparation of high-density spherical nickel hydroxide

Spherical nickel hydroxide was prepared by feeding an aqueous solution containing Ni sulphate doped with Cd, Co and Zn sulphates into a 5 L reactor, accompanied by the addition of aqueous NaOH to regulate the pH value and aqueous ammonia as complexing agent to control the degree of supersaturation of $\text{Ni}(\text{OH})_2$ in the solution. The conditions were as follows: 1.5 M NiSO_4 , pH \approx 11, $[\text{NH}_3]/[\text{Ni}^{2+}] \approx$ 1, $T \approx$ 60 °C, Co doped 1%, Zn doped 1.5%, Cd doped 1.5% (wt.%, based on Ni), mixing

speed \approx 150 rpm and feed rate \approx 10 mL/min. Nickel hydroxide was removed continuously from the reactor, then washed and dried.

2.6. Analysis

The concentrations of metals in the aqueous solutions were measured by atomic absorption spectrophotometer (TAS-990). Those in the organic phase were calculated from the mass balance. The pH was measured with a TOA pH meter type HM-30S. XRD was measured on D/MAX-RB X-ray powder diffractometer and SEM images were obtained using a Hitachi S-450 Scanning Electron Microscope. The specific capacity of the spherical $\text{Ni}(\text{OH})_2$ was measured by a Land Charge/Discharge Tester.

3. Results and discussion

3.1. Leaching

The rare earths in the spent Ni–MH batteries are mainly light rare earths, such as La, Ce, Pr and Nd. The solubility of rare earth sulphates obviously reduces with rising temperature (Xu, 2002), as shown in Fig. 1. Whereas, the solubilities of NiSO_4 , CoSO_4 , MnSO_4 , FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ are high enough at room temperature and generally increase with rising temperature up to 100 °C.

Based on the differences in the solubility characteristics between the sulphates of rare earths and those of cobalt, nickel etc, higher concentrations of H_2SO_4 and lower liquid to solid ratios were adopted in the leaching process to ensure the precipitation of most of the rare earths in the leach residues. Fig. 2 shows the effect of temperature on the leach efficiency for different metal ions under the following fixed conditions: H_2SO_4 , 3 M; leaching time, 4 h; liquid–solid ratio, 7.5:1. Whilst the leach efficiency of the rare earths decreased with rising temperature, the leach efficiency of the other metals remained high and could reach 99% at 95 °C because their solubility was sufficient. After leaching for 4 h at 95 °C, only 5% rare earths entered into the leach liquor which contained (g/L) 60.9 Ni, 0.80 RE, 5.07 Co, 1.69 Mn, 2.19 Zn and 0.34 Fe.

3.2. Separation of impurities and rare earths from nickel and cobalt

The $\text{pH}_{1/2}$ values (defined as the pH at which 50% metal extraction occurs) of P204 for RE^{3+} , Fe^{3+} , Zn^{2+} and Mn^{2+} in sulphuric acid lie below 2.5 (Sato et al., 1978; Grimm and Kolarik, 1974; Ritcey and Ashbrook, 1979; Nathsarma and Devi, 2006; Ritcey, 1983), whereas the $\text{pH}_{1/2}$ values of Co^{2+} and Ni^{2+} were 3.6 and 3.9 respectively (Devi et al., 1998). Therefore, the separation of impurities and rare earths from cobalt and nickel can be realized through solvent extraction with P204.

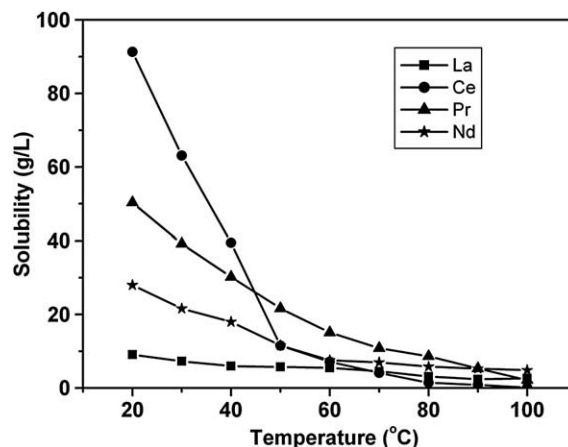


Fig. 1. Solubility-temperature curve of rare earth sulphates.

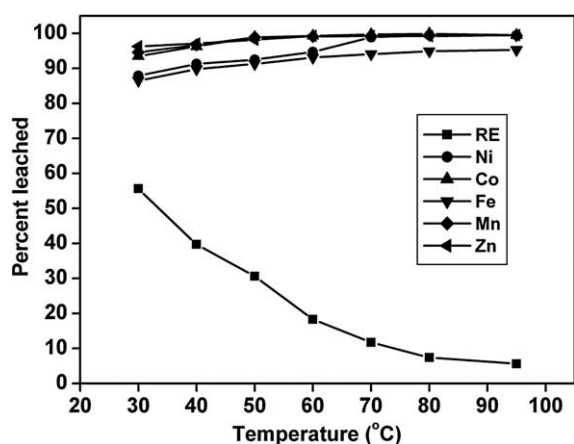


Fig. 2. Relationship between leach efficiency and temperature.

Table 1 shows the effect of equilibrium pH on the single-stage extraction of metal ions in the actual leach liquor with 20% P204 at an O:A ratio of 1:1. Most of the rare earths, iron(III) and zinc could be removed by a single-stage extraction at pH = 2.5, but the removal of manganese was insufficient. Hence, a multi-stage counter-current operation was needed to remove manganese thoroughly.

In order to determine the required number of extraction stages, a McCabe–Thiele equilibrium isotherm was determined for the extraction of manganese by 20% P204 at an equilibrium pH of 2.5 as shown in Fig. 3. According to this diagram, the aqueous feed liquor required a five-stage counter-current extraction at an O:A ratio of 1:1 on the assumption that the stage efficiency was 80%. After carrying out a five-stage counter-current extraction at pH 2.5, the concentration of rare earths, Mn, Zn and Fe in the raffinate decreased to below 0.01 g/L and about 3.5% Co and 0.1% Ni were co-extracted into the organic phase.

3.3. Scrubbing of cobalt and nickel

The small amount of cobalt and nickel co-extracted into the organic phase was easily eliminated through a 3-stage counter-current scrubbing with 0.1 M H_2SO_4 at an O:A ratio of 20:1, resulting in a scrub solution containing (g/L) 3.55 Co, 1.21 Ni, 0.7 Mn, 0.1 Zn which was merged into leach liquor. After scrubbing, the concentrations of Co and Ni in the organic phase were below 0.01 g/L.

3.4. Scrubbing of zinc and manganese

In order to recover the rare earths in the organic phase, Zn and Mn should be first removed by scrubbing. Unlike the rare earths and Fe (III), the impurity Zn and Mn were easily scrubbed and completely removed in a 5-stage counter-current scrubbing operation carried out at an O:A ratio of 10:1 with 0.5 M H_2SO_4 as the scrubbing agent. The scrubbing liquor contained (g/L) 21.4 Zn, 16.7 Mn, 0.1 RE. The removal efficiency for Zn and Mn were 97.7% and 98.8%.

Table 1
Effect of equilibrium pH on extraction metal ions with 20% P204 in kerosene (O:A = 1:1).

Equilibrium pH value	Extraction of metal ions (%)					
	RE ³⁺	Zn ²⁺	Mn ²⁺	Fe ³⁺	Co ²⁺	Ni ²⁺
1.0	71.4	37.9	5.2	87.1	0	0
1.5	78.2	61.4	16.5	92.3	0.9	0
2.0	87.6	72.3	28.3	94.5	2.9	1.1
2.5	91.4	84.6	56.7	97.8	4.7	2.3
3.0	94.9	89.2	61.5	98.2	11.3	8.5
3.5	95.1	92.1	69.7	98.9	36.7	25.2

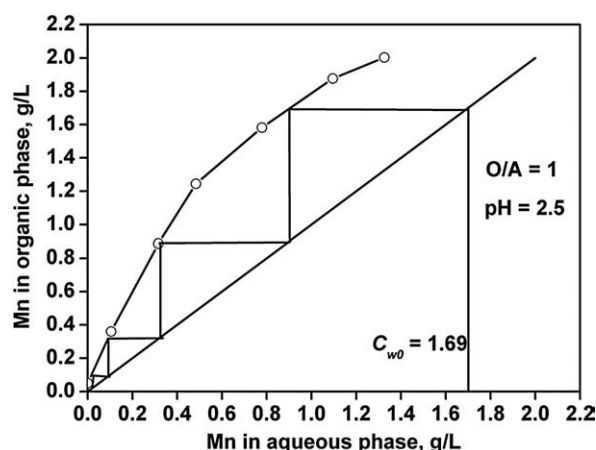


Fig. 3. McCabe–Thiele equilibrium isotherm for the extraction of manganese with P204 at pH 2.5.

3.5. Stripping of rare earths and iron

The rare earths loaded in the scrubbed organic phase could be stripped with 2 M HCl by using 5-stage counter-current extraction at an O/A ratio of 10:1, resulting in a stripping liquor containing (g/L) 7.7 RE and a similar high concentration of HCl. The small amount of iron (III) loaded in the organic phase could only be completely removed by concentrated hydrochloric acid because P204 coordinates with Fe^{3+} at very low pH values. The actual organic phase was processed by 6 M HCl in a 4-stage counter-current stripping at an O/A ratio of 20:1, resulting in the organic phase containing <0.001 g/L Fe. The strip liquor together with a proper amount of HCl solution was used to dissolve $\text{RE}(\text{OH})_3$ as discussed below.

3.6. Recovery of rare earths

Because the solubility of rare earth sulphates was neither high nor low at room temperature, direct dissolution of the leach cake with HCl, followed by evaporation of the filtrate would lead to a mixture of RESO_4 and RECl_3 as products. For this reason, the leach cake containing the majority of rare earths was dispersed in water at a liquid–solid ratio of 5:1 and then 1.1 times the theoretical amount of NaOH was added to this suspended liquor to completely transform the rare earth sulphates to insoluble $\text{RE}(\text{OH})_3$. The $\text{RE}(\text{OH})_3$ precipitate together with small amount of insoluble organic adhesive from the battery's negative electrode was filtered. The resulting filter residue was then processed with the rare earths strip liquor and a proper amount of adventitious HCl. Finally, the insoluble organic adhesive was filtered, resulting in a pure RECl_3 solution from which pure rare earth chlorides were crystallized after evaporation. The overall recovery of rare earths was about 97.8%.

3.7. Separation and recovery of nickel and cobalt

It has been known for some time that the separation of nickel and cobalt can be achieved by using organo-phosphorus acids, i.e. D2EHPA (P204), PC-88A (P507) and Cyanex 272 (Danesi et al., 1985; Rickelton et al., 1984; Robertson, 1983). The difference in $\text{pH}_{1/2}$ value between cobalt and nickel increases in the following sequence: P204 < P507 < Cyanex 272, which indicates that the separation ability for cobalt and nickel ascends from D2EHPA, PC-88A to Cyanex 272. For example, when 0.1 mol/L P204, P507 and Cyanex 272 are used to separate cobalt and nickel (2.5×10^{-2} mol/L) at pH 4 at 25 °C with the O/A ratio of 1:1, the separation coefficients ($\beta_{\text{Co/Ni}}$) are 14, 280, and 7000 respectively. Nevertheless, the saturated capacity for cobalt descends in the following sequence: P204 > P507 > Cyanex

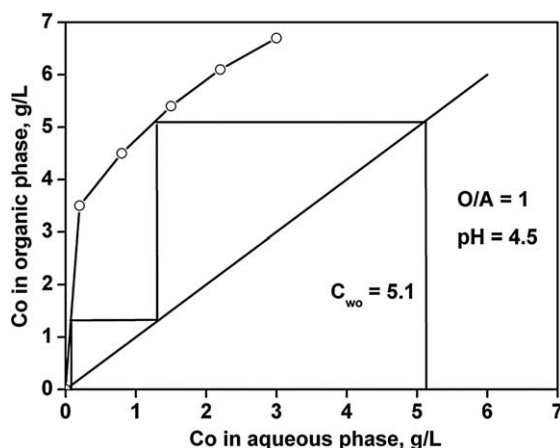


Fig. 4. McCabe–Thiele equilibrium isotherm for the extraction of cobalt with Cyanex 272 at pH 4.5.

272 (Preston, 1982). So, separation coefficient, saturated capacity, the composition of the feed liquor and price should all be taken into account to determine which organo-phosphorus acid is used.

In general, when the Co/Ni ratio is around 1/1 and there is much impurity, such as Zn, Mn and Cu, that needs to be removed, P204 is used to remove impurity and separate Ni and Co. But when the Co/Ni ratio is lower than 1/5, too many stages are needed for P204, and P507 is more suitable. When Co/Ni is lower than 1/10, Cyanex 272 can reduce the number of extraction stages greatly and improve the recovery rate. Hence, Cyanex 272 was used to separate cobalt from nickel in this study.

In order to determine the number of extraction stages, a McCabe–Thiele equilibrium isotherm was determined (Fig. 4) for the extraction of cobalt with 20% Cyanex 272 at pH 4.5. According to the McCabe–Thiele diagram, the concentration of cobalt in the aqueous phase could be reduced to <0.01 g/L by two-stage counter-current extraction with 20% Cyanex 272. As for the actual feed liquor after the removal of rare earths and other impurities, a three-stage counter-current extraction was carried out, assuming a stage efficiency of about 80%, which decreased cobalt in the raffinate to 3 mg/L. Then the loaded organic phase was scrubbed with 0.1 M H₂SO₄ at an O/A ratio of 10:1 and the scrub solution was merged into the leach liquor. The overall percentage extraction of cobalt reached >99.9% with almost no extraction of nickel.

Cobalt loaded on the organic phase was easily stripped with 1 M H₂SO₄ in a single stage and hydrated CoSO₄ and NiSO₄ crystals with high purity were obtained after evaporation of the stripping liquor

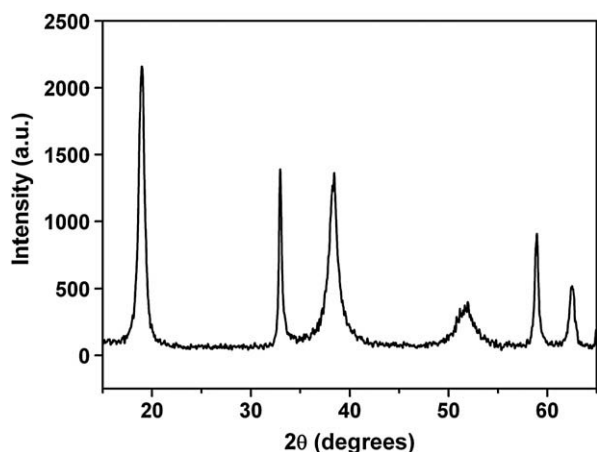


Fig. 5. X-ray diffraction pattern of the as-prepared spherical nickel hydroxide.

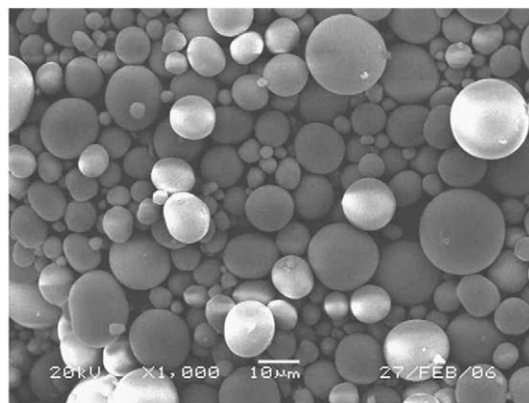


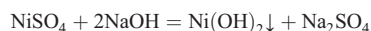
Fig. 6. SEM images of the as-prepared spherical Ni(OH)₂ sample.

and raffinate respectively. The overall recovery rates of cobalt and nickel were both about 98.1%.

3.8. Preparation of spherical nickel hydroxide

In order to improve the added value of the recovery products, nickel sulphate was used as a starting material to prepare spherical nickel hydroxide which is the positive active materials of Ni–MH batteries. Elemental analysis showed that the recovered NiSO₄ starting material contained (wt.%) 0.23% Co, 0.04% Mn, 0.03% Zn, 0.01% RE and 0.01% Fe.

The preparation reaction for nickel hydroxide is as follows:



$$K_{\text{sp}} = [\text{Ni}^{2+}] \cdot [\text{OH}^-]^2 = 2.02 \times 10^{-15}.$$

Because the solubility product (K_{sp}) of Ni(OH)₂ is so small, it is difficult for Ni(OH)₂ crystals to grow because nucleation is too rapid. To overcome this, Jiang et al. (1997) developed a “controlled crystallization method” to prepare spherical nickel hydroxide powders with high density. With this method, the concentration of OH[−] was controlled by alkali liquor, and the activity of Ni²⁺ was controlled by ammonia complexation. In addition, many research have confirmed that the doping of a small quantity of other metal ions, such as Co, Zn and Cd, could improve the reversibility and cycle life of Ni(OH)₂ due to the lattice defect caused by the doped cations (Masahiko et al., 1991). Therefore, several factors such as pH value, concentrations of starting materials, temperature, mixing speed and feed rate, exert a great influence on the electrochemical properties of the final product.

By reference to many previous research results (Armstrong and Charles, 1989; Li et al., 1998; Vidotti et al., 2009; Zhang et al., 2009), a typical preparation procedure was performed (see Experimental section) to obtain spherical nickel hydroxide with good electrochemical performance.

The XRD pattern (Fig. 5) indicated that the as-synthesized product crystallized in P-3m1 space group (β-Ni(OH)₂) and no other phase occurred. Elemental analysis showed that the product contained 0.9% Co, 1.2% Zn, 1.4% Cd, 0.005% Mn, 0.01% RE and 0.008% Fe. (wt.%, based on Ni), which indicated that Co, Zn and Cd had entered into the crystal lattice of Ni(OH)₂. Almost no sulphur was found in the Ni(OH)₂

Table 2
Physicochemical and electrochemical data of the as-prepared nickel hydroxide.

Item	Loose density (g cm ^{−3})	Tap density (g cm ^{−3})	Grain size (μm, D50)	Specific surface (m ² g ^{−1})	Specific capacity (mAh g ^{−1})
Standard	≥1.65	≥2.10	10–18	20.0 ± 5.0	≥195
Measured	1.93	2.27	12.49	21.03	198

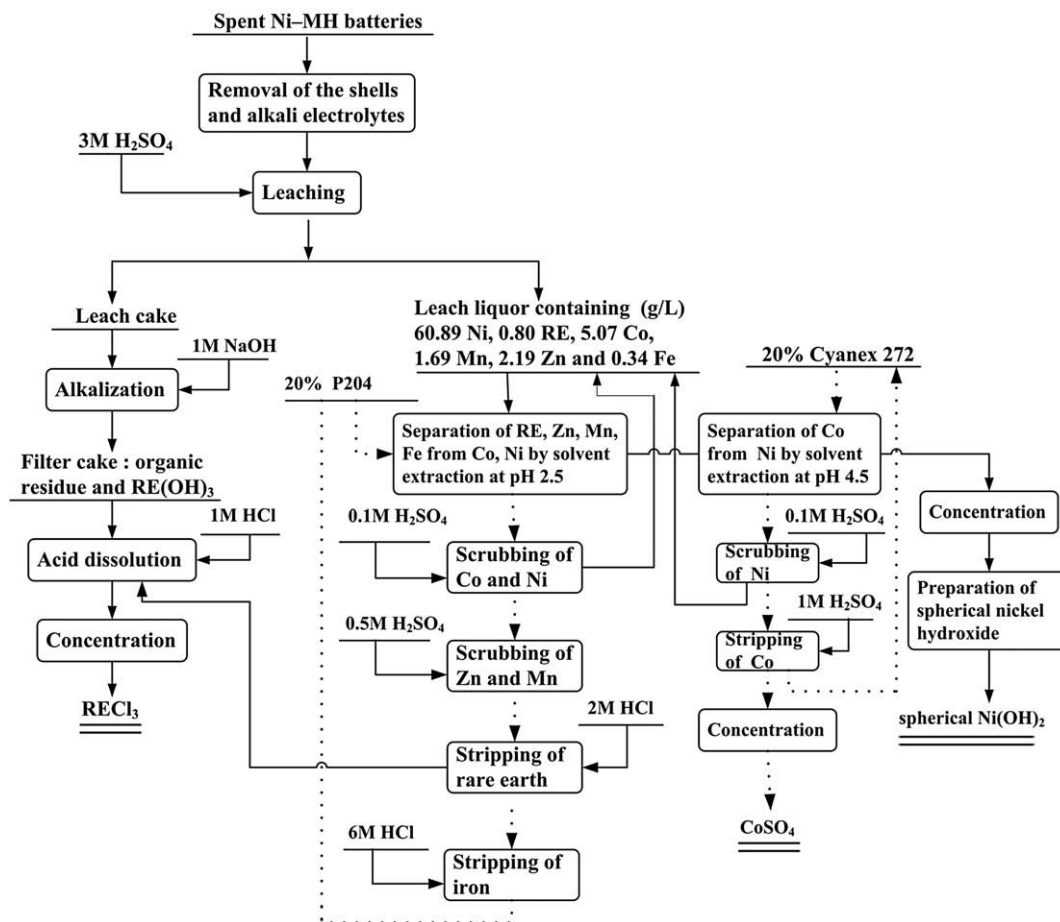


Fig. 7. Overall flowsheet for recovery of Ni, Co and RE and preparation of spherical $\text{Ni}(\text{OH})_2$ from spent Ni-MH batteries.

product, which indicated that no basic nickel sulphates formed under such conditions. The SEM image (Fig. 6) showed that the product was composed of spherical or ellipsoidal nickel hydroxide particles with wide size distribution from $3\mu\text{m}$ to $20\mu\text{m}$, which was beneficial to improve the specific energy of the nickel electrode. The physico-chemical and electrochemical data are given in Table 2.

4. Conclusions

A hydrometallurgical procedure including leaching, solvent extraction, evaporation and crystallization has been performed to recover rare earths, nickel and cobalt from the spent Ni-MH batteries. By using the recovered nickel sulphate as starting material, spherical nickel hydroxide doped with Co, Zn and Cd was prepared with wide size distribution under strict control of the reaction conditions. An overall flowsheet for recovery of Ni, Co and RE and preparation of spherical $\text{Ni}(\text{OH})_2$ from spent Ni-MH batteries is presented in Fig. 7.

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